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Nuclear quadrupole interaction at Fe-57 in semimetals arsenic and bismuth

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Abstract Nuclear quadrupole interaction at iron impurities in arsenic and bismuth semimetals were measured using iron Mossbauer spectroscopy. From the quadrupole splitting values, the electric field gradient in arsenic is evaluated to be 8.42(22) x 10^{17} V/cm^2 and 3.87(12) x 10^{17} V/cm^2 for bismuth. The ratio of electronic contribution of electric field gradients to ionic contribution is found to be larger than that normally found in *sp* metals. In general the electron contributions follow the trend set by the electron densities in these metals. However, the magnitudes of electric field gradient are not consistent with electron densities.

Keywords Quadrupole interaction, Fe-57 Mossbauer, Bi, As

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1. Introduction

Group VA semimetals (arsenic, antimony and bismuth) in bulk form, films, alloys and nano-wires are industrially important materials for use as thermoelectric materials, dopants for semiconductors *etc.* [1-3]. Study of electric field gradients [EFG] gives information about the symmetry around the probe atom. This can in turn, be used to study defects [4]. Even though there exist many quadrupole interaction studies at different impurity probes in normal non-cubic metals [5-7], only little is known about EFG in group VA semimetals. These semimetals offer a suitable system for the study of different contributions to the EFG at different probe sites since they are isostructural. The rhombohedral structure of arsenic, antimony and bismuth is only a slight distortion from a simple cube. Hence, they provide a strong illustration of the crucial importance of the crystal structure in determining metallic properties. Earlier quadrupole interaction studies [8-15] in some of these semimetals showed that the systematic trends of the EFG generally found in metals are also valid in them. But the temperature variation of ^{111}Cd in antimony showed an anomalous behaviour [14]. Further, it was observed that the temperature dependence of the EFG at ^{57}Fe probe in antimony metal does not follow the usual $T^{3/2}$ behaviour [15]. On the other hand, the ^{57}Fe in Te [16] and Se [17] were found to follow the $T^{3/2}$ behaviour in spite of their complicated spiral structure and the covalent bonding between the host atoms.

Out of the group V semimetals, bismuth and arsenic are the least studied hosts. In particular, the EFG studies at different impurity probes in bismuth host are important because of the fact that bismuth has a less distorted structure and less band overlap than that of arsenic and antimony. The electron density in bismuth is only 1000 times lower than that in arsenic semimetal. Hence, EFG studies using different impurity probes will be important for understanding the origin of EFG in semimetals. In this paper, we report nuclear quadrupole interaction studies at ^{57}Fe in bismuth and arsenic semimetal using Mössbauer spectroscopy.

2. Experimental

High purity arsenic and bismuth (99.999%) and enriched iron-57 were used to make ^{57}FeAs and ^{57}FeBi samples containing 0.5 atomic percent iron. The required proportions of materials were sealed in thick quartz tubes under vacuum of 10^{-5} torr. The arsenic samples were prepared by heating at 1100 K for about 6 days and Bi samples by heating at 1000 K for about 6 days. After the heat treatment, the samples were quenched into water. X-ray analysis showed diffraction patterns identical to pure arsenic and bismuth for these samples.

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A Mössbauer spectrometer in the constant acceleration fly-back mode and a 25 mCi ^{57}Co(Pd) source were used for recording the Mössbauer spectra of the samples. The absolute velocity of the source was measured by using He-Ne laser interferometer. A natural iron spectrum recorded by the spectrometer showed a line width of 0.22mm/sec. The Mössbauer spectra were first recorded over a velocity range of 15mm/sec velocity range to check for the presence of any magnetic phases. Since no magnetic phases were observed, further spectra were recorded for a range of 6mm/sec. Since the non-resonant absorption of 14.4 keV gamma rays is large in bismuth compared to that in arsenic, the counting rate was low for the bismuth. The Mössbauer data were computer analyzed using a least squares fit program.

3. Results and discussion

The Mössbauer spectra of the ^{57}FeAs and ^{57}FeBi system containing 0.5 atomic percent iron at room temperature are given in Figure 1. The Mössbauer parameters of these samples obtained from least square analysis, are given in Table 1. The isomer shift values are with reference to natural iron. The errors are given parenthetically in each case. The line width obtained for ^{57}FeAs system is 0.32(2) mm/sec whereas that for ^{57}FeBi system is 0.52(3). The large line width observed for ^{57}FeBi system compared to that normally observed for ^{57}Fe diffused into metallic hosts may be due to distribution of Fe atoms into substitutional as well as interstitial positions in bismuth. Computer analysis of Mössbauer spectra of ^{57}FeBi system assuming two quadrupole doublets, did not give a satisfactory fit. This indicates that the EFG arising from the substitutional as well as non-substitutional sites are not sufficient to show two discrete Mössbauer doublets corresponding to each of these sites. Anila *et al* [18] obtained a broad line doublet for ^{57}Co diffused into the bismuth system with a line width of 0.76(1) mm/sec. This large line width observed may be due to the improper diffusion of cobalt atoms and interaction of the probe atoms with the different impurities introduced into the bismuth during the electroplating and temperature treatment. It can be seen from the Mössbauer studies of ^{57}FeSb [15] and ^{57}FeSi [19] that the line width is small in samples prepared by diffusing ^{57}Fe atoms (absorber studies) when compared to that prepared by diffusion of ^{57}Co activity (source studies). Since the line width observed for ^{57}FeAs system is same as that found for iron atoms diffused into metals, it is reasonable to assume that iron atoms are occupying substitutional sites in arsenic.

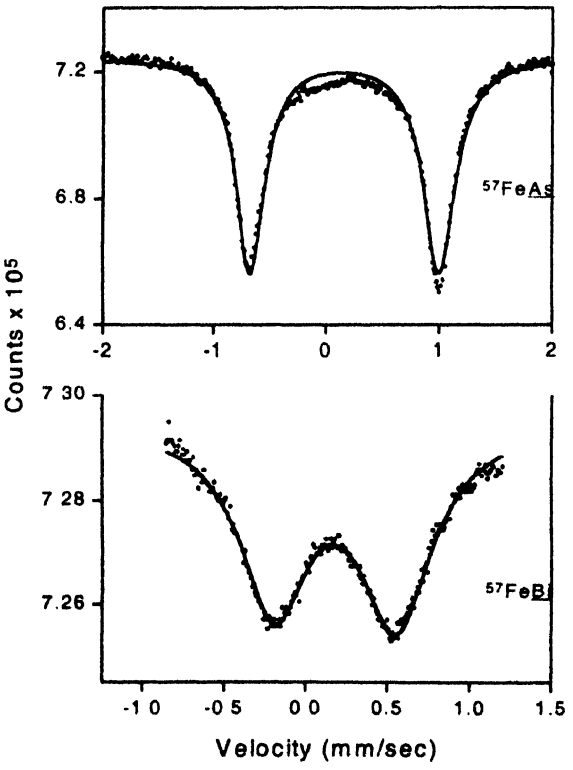

Figure 1. The Mössbauer spectra of ^{57}FeAs and ^{57}FeBi system containing 0 5 at.% iron-57 at room temperature.

Table 1. Mössbauer parameters of arsenic and bismuth containing 0.5 at% of Fe-57

Host	Isomer shift (mm/sec)	Quadrupole splitting (mm/sec)	Line width (mm/sec)
Arsenic	0.31(2)	1 68 (2)	0 32(3)
Bismuth	0 39(3)	0 77(2)	0 52(3)

The quadrupole splitting and isomer shift observed in the present study for ^{57}FeBi are different from that reported for the ^{57}Co diffused Bi samples. The quadrupole splitting reported from the source studies [18] is 0.55mm/sec and is much less than the quadrupole splitting of 0.77(2) mm/sec observed in the present study. Such a difference between source and absorber studies was also observed in the case of Sb [15, 19]. In the case of ^{57}FeSb system prepared by diffusing ^{57}Co activity into antimony matrix, only a broad singlet was observed [19] But when the sample was prepared by diffusing ^{57}Fe atoms into antimony matrix [15], a quadrupole splitting of 1.32mm/sec was observed. This difference in the results obtained from the source and absorber studies in antimony shows that ^{57}Co atoms may be going into grain boundaries and this yields a broad singlet whereas ^{57}Fe atoms diffused into the host occupy a definite lattice position in the matrix.

The energy level splitting observed in ^{57}Fe Mössbauer spectroscopy can be related to electric field gradient by :

$$\Delta E_Q = \frac{e^2qQ}{2}\left[1+\frac{1}{3}\eta^2\right]^{1/2}, \qquad (1)$$

where eq is the electric field gradient, Q the quadrupole moment of 14.4 keV state of ^{57}Fe and η is the asymmetry parameter. Since arsenic and bismuth crystallize in the rhombohedral structure, the asymmetry parameter will be zero for iron atoms sitting in the substitutional position. Taking Q = 0.192 (18) b [20], the EFG at room temperature is evaluated to be 8.42(22) x 10^{17} V/cm^2 for ^{57}FeAs and 3.87(12) x 10^{17} V/cm^2 for ^{57}FeBi. The

experimentally observed EFG is related to the electronic part of the EFG by the relation

$$eq_{exp} = eq_{latt}(1 - Y_\infty) + eq_{el}. \quad (2)$$

The ionic model calculations by Taylor and Hygh [21] gives $eq_{latt} = -0.192 \times 10^{17}$ V/cm^2 for arsenic and -0.039×10^{17} V/cm^2 for bismuth at room temperature, assuming the normal valence for As and Bi as +5. Taking $(1 - Y_\infty) = 10.14$ for iron [22], we get $eq_{ion} = eq_{latt}(1 - Y_\infty) = -1.95 \times 10^{17}$ V/cm^2 for ^{57}Fe in As and -0.395×10^{17} V/cm^2 for ^{57}Fe in Bi. Since it is not possible to obtain sign of experimentally observed EFG from the present study, assuming a positive value for the eq_{exp}, the electron contribution to the total EFG is evaluated to be $eq_{el} = 10.37 \times 10^{17}$ V/cm^2 and 4.26×10^{17} V/cm^2 for ^{57}Fe in As and Bi respectively.

According to the universal correlation proposed by Raghavan *et al* [23],

$$eq_{el} = -K\, eq_{ion}, \quad (3)$$

where K is constant and is of the order of 3. From the present data on ^{57}FeAs system, the value of K comes out to be about 5 and that for ^{57}FeBi is 10. The higher value of K, obtained for As and Bi in the present study when compared to that observed in normal metals [20], may be understood as due to the presence of the local electronic contribution to the EFG arising from the covalency effects in the binding of the host atoms.

The ionic (eq_{ion}) and electronic (eq_{el}) contribution to the total EFG in group VA semimetals for different impurity probe systems as well as for pure systems are tabulated in Table 1. The eq_{latt} values are taken from Ref.[21] and $(1 - Y_\infty)$ values for different probe ions are from the tabulation of Feiock and Johnson [22]. The sign of EFG is not available for any of the above systems. Hence, the electron contributions were evaluated assuming both positive (eq_{el}^1) as well as negative sign (eq_{el}^2) for the eq_{exp}. The ratio $K = \dfrac{eq_{el}^1}{eq_{ion}}$ for the pure systems exceed the value proposed by Raghavan *et al* [23]. K does not follow the probe valency dependence [24] for many impurity systems. This shows that in semi metals, the electronic contribution to the EFG is larger than that normally found in most of the *sp* metals. This can be understood in terms of a possible contribution to the EFG due to the covalency effects in the binding of the host atoms. The values of eq_{el}^2 evaluated assuming a negative sign for eq_{exp} show that the semimetals do not follow the positive (k = +2) correlation proposed by Ernst *et al* [27].

Since the semimetals As, Sb and Bi are isoelectronic, it is interesting to see the behaviour of the electronic contribution for different probes in these hosts. In Figure 2, the electronic contribution to the total EFG, eq_{el}^1 are plotted for different probes against As, Sb and Bi. From the figure, it can be seen that for a given probe, the electron contribution decreases as one moves from As to Bi except for the case of In probe where one can see a small increase in bismuth host than at Sb host. The electron densities change by one order of magnitude between As and Sb and by three orders of magnitude between As and Bi; whereas the eq_{el} follows nearly a smooth variation from As to Bi. This difference may be attributed to the presence of strong local contribution in these hosts.

Table 2. Quadrupole interactions for different probes in semi metals As, Sb and Bi. eq_{el}^1 and eq_{el}^2 are the calculated values assuming the total EFG to be positive and negative, respectively. All the values eq_{exp} are taken from [24] unless otherwise noted. Techniques used are available in the reference. Values of Y_∞ are from [22]. The value of eq are in units of 10^{17} V/cm^2.

Host	Probe	eq_{exp}	eq_{latt}	eq_{el}^1	eq_{el}^2	$\dfrac{eq_{el}^1}{eq_{ion}}$
As	^{57}Fe	± 8.42[a]	- 1.95	+10.37	- 6.47	5.3
	^{75}As	+ 6.48	- 1.24	+ 7.72	- 5.24	6.2
	^{111}Cd	± 5.91	- 5.82	+11.73	- 0.09	2.0
	^{119}In	± 0.51	5.00	+ 5.51	+4.49	1.1
	^{181}Ta	±13.97[c]	-11.90	+25.87	2.07	2.1
	^{204}Pb	± 3.95	- 9.94	+13.89	+5.99	1.3
Sb	^{57}Fe	± 6.29[b]	- 0.52	+ 6.81	5.77	13.0
	^{69}Ge	± 3.50	3.21	+ 6.71	0.29	- 1.9
	^{99}Ru	±14.20	0.92	+15.12	13.28	16.5
	^{111}Cd	± 5.43	- 1.54	+ 6.97	+3.89	4.5
	^{119}Sn	± 3.10	- 1.16	+ 4.26	1.94	- 3.6
	^{119}In	± 1.14	- 1.30	+ 2.44	+0.16	1.8
	^{121}Sb	±11.39	0.67	+12.06	+10.72	- 18.0
	^{181}Ta	± 7.82[c]	3.10	+10.92	- 4.72	- 3.5
	^{197}Hg	± 8.32	- 3.06	+11.38	+5.26	- 3.7
	^{204}Pb	± 2.02	- 2.59	+ 4.61	+0.57	- 1.7
Bi	^{57}Fe	± 3.87[a]	- 0.39	+ 4.26	3.48	- 10.7
	^{69}Ge	± 1.71	- 2.51	+ 4.22	- 0.80	- 1.7
	^{111}Cd	± 4.00	- 1.19	+ 5.19	+2.81	- 4.3
	^{119}In	± 2.54	- 1.02	+ 3.56	+1.52	- 3.5
	^{121}Sb	± 7.34	- 0.53	+ 7.87	- 6.81	15.0
	^{181}Ta	± 4.70[d]	- 2.44	+ 7.14	+2.26	- 2.9
	^{204}Pb	± 1.07	- 2.02	+ 3.09	- 0.95	- 1.5
	^{209}Bi	± 5.31	- 1.89	+ 7.20	- 3.42	- 3.8

[a] Present work
[b] Reference [15] (Mossbauer study)
[c] Reference [11](TDPAC study)
[d] Reference [12] (TDPAC study)
[e] Reference [25] (TDPAC study)

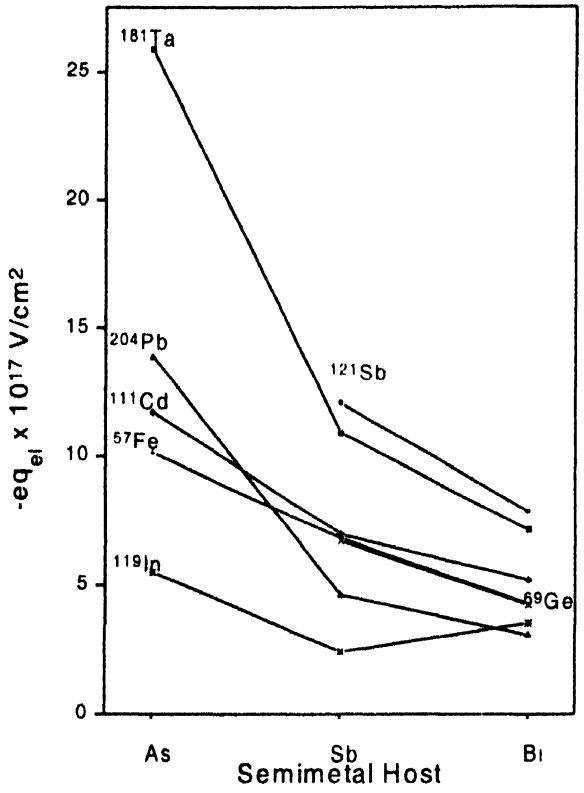

Figure 2. Electronic contribution of EFG for different probes in semimetals As, Sb and Bi

4. Conclusion

The electric field gradient at room temperature obtained for ^{57}Fe in As and Bi semimetals show that the electronic contribution to EFG at iron impurity sites in these hosts are more compared to that in normal metals. Analysis of the EFG data for different impurities in these hosts shows that neither the universal correlation nor probe dependence of EFG is followed in general, in semimetallic hosts. Though in general, the electron contributions follow the trend set by the electron densities in these hosts, the magnitudes of EFG are not consistent with electron densities.

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